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(54) PRESSURE SENSITIVE ADHESIVE COATED LAMINATE AND METHOD FOR MAKING SAME

(71) We, UNITED MERCHANTS AND MANUFACTURERS INC., of 1407 Broadway, New York. New York 10018, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention pertains to laminates having a pressure sensitive adhesive layer. More particularly, this invention relates to pressure sensitive adhesive coated laminates for covering substrates for decorative and/or protective purposes or for adhesive tapes, labels, and the like products.

The development of pressure sensitive adhesive systems has resulted in their use in a great variety of areas, such as, for tapes, decals, decorative and protective coverings in sheet form for walls, furniture, and the like articles, self-stick floor coverings, and generally, for any purpose wherein it is desired to adhere an article to a substrate.

Because of the increased movement towards the so-called "do-it-yourself" type of home improvements and decorating, many articles, such as, wall coverings, counter coverings, tile appliques, shelving covers and edgings, and the like, are now sold with pressure sensitive adhesive coatings thereon. Such pressure sensitive adhesive coatings facilitate the application of such articles to the desired substrate by eliminating the need to apply a separate adhesive or to utilize another type of securing device, such as nails, screws or staples.

One of the problems with such pressure sensitive adhesive coated articles is that, in use, they are extremely difficult to position and, if necessary, reposition, even immediately after the application to the substrate. This problem is particularly severe with articles which are in the form of decorative and protective sheets coated with a pressure sensitive adhesive and which are used to cover substrates, e.g., walls, cabinet tops or furniture. Very often, such sheets or laminates possess decorative patterns on the outer face and it is important that the proper matching of the patterns from adjacent sheets be obtained. Moreover, it is often important that the seams between adjacent sheets be straight, uniform, and parallel.

Another problem which arises, particularly with larger pieces or sheets, such as, when one is attempting to cover a large piece of furniture or large wall area, is the difficulty in handling the sheet and the avoidance of touching of one area of the pressure sensitive adhesive coated side of the sheet with another area of the same side. When this occurs, the sheet will fold and the respective touching areas must be pulled apart. This can become extremely cumbersome, particularly with large sheets.

It also can result in removal of areas of the pressure sensitive adhesive coating when an attempt is made to pull the touching areas apart and cause discontinuities of the pressure sensitive adhesive coating as well as produce torn, stretched or wrinkled areas in the facing sheet which is usually made from paper or plastics sheeting or film.

Additionally, on application of the laminate to a substrate, folds, wrinkles, and bubbles often appear. These are relatively difficult to remove because of the aggressiveness of the pressure sensitive coated sheet for the substrate. This can be particularly troublesome when the facing layer is relatively thin, such as, for example, a thin film of vinyl resin.

The difficulty of handling the larger size sheets is further increased by their affinity for picking up electrostatic charges. This problem often makes it very cumbersome to keep the sheet from touching the substrate, e.g., a wall, before the sheet is properly positioned. Once the sheet has

touched the wall, it is difficult to remove and replace it in the proper position.

The present invention seeks to provide a laminate of the type comprising a facing layer, generally of a decorative or protective material, and a layer of a pressure sensitive adhesive adjacent to one surface thereof, with which the above noted problems attendant to the commercially available laminates of this type are minimized.

Particularly, applicants have discovered that by depositing on the surface of the pressure sensitive adhesive layer, a substantially uniformly distributed, discontinuous layer of a material possessing certain chemical and physical properties as defined hereinafter, a pressure sensitive adhesive laminate is obtained which is easily positioned and adhered to the substrates, and which can be removed, and, if necessary, repositioned with ease ~~during~~ the application time.

repositioned

The material used as the discontinuous layer is a polysiloxane, as defined hereinafter. It is non-tacky, but is of an appropriate molecular weight so that it is, by itself coatable, or can be rendered coatable, e.g., by dilution or emulsification, for purposes of manufacture of the laminate.

As with the commercially available laminates, it is preferred to provide laminates embodying the present invention with a backing sheet or other layer having a release surface adjacent to the pressure sensitive adhesive layer. When a release surface is present, the polysiloxane layer is interposed as an interlayer between the layer having the release surface and the pressure sensitive adhesive layer.

By virtue of the effect which the interlayer material exerts on the pressure sensitive adhesive, the laminate, at the time of removal from the release surface, i.e., when it is about to be applied to the substrate, possesses a relatively low peel value, i.e., a low degree of affinity for the substrate. As a consequence, if, when applied to the substrate, the particular sheet is not straight or in the desired position, it is easily removed for repositioning. Moreover, if two areas of the pressure sensitive adhesive coated face of the sheet should touch one another, they are easily pulled apart without disturbing the uniformity of the coating of the pressure sensitive adhesive or stretching or wrinkling of the facing layer.

Furthermore, any air bubbles or wrinkles which occur in the laminate on application to the substrate, may be easily removed by smoothing with hand pressure.

The present invention will now be described by way of example with reference to the accompanying drawings, in which:—

Figures 1, 2, 3, 4. and 5, are sequential cross-sectional diagrams illustrating the formation of a laminate in accordance with the present invention.

Figure 6 is a schematic drawing of a process in accordance with the present invention.

Figure 7 is a drawing similar to Figure 6 of another process in accordance with the present invention.

Figure 8 is a drawing similar to Figure 6 of yet another process in accordance with the present invention.

Figure 9 is a photograph of the pressure sensitive adhesive coated side of the laminate 18 shown in Figure 5.

Figure 10 is a photograph of droplets 12 on layer 10 shown in Figure 2.

Figure 11 is a graph of peel values determined at different aging times on an acrylic-coated test surface for laminates prepared using different laminating pressures.

Figure 12 is a graph showing the variation in peel value with residence time on an acrylic-coated test surface for samples prepared using varying concentrations of polysiloxane material and zero laminating pressure.

Figure 13 is a graph showing the change in peel value with resident time on an acrylic-coated test surface for samples prepared using varying concentrations of polysiloxane material with a 165 line quadrangular cell gravure roll.

Figure 14 is a graph similar to that of Figure 11 wherein a 120 line quadrangular cell gravure roll was used.

Figure 15 is a graph similar to that of Figure 11 wherein an 80 line quadrangular cell roll was used.

Figure 16 is a graph showing the variation in peel value with resident time on an acrylic coated test surface for samples prepared using a 10% concentration by weight of polysiloxane material and gravure rolls having different cell volumes.

Referring to the Figures, Figure 1 shows a conventional backing layer 10 used for pressure sensitive adhesive laminate. This material is generally referred to as a release sheet, although, in actuality, it may be fabricated from two separate components, namely a supporting sheet, such as, kraft paper or other material having sufficient dimensional stability to act as a supporting sheet, and a coating of a release material thereon. Such sheets may also be impregnated with the release material.

The most well known and economical type release sheet used presently is an unbleached kraft paper directly coated on one or both faces with a cured silicon. It is

possible, however, to use other release materials, such as, glassine papers, spun bonded synthetic nonwovens, e.g., polyethylene, or continuous films of extruded synthetics, e.g., polyesters, polyethylene or polypropylene, and Cellophane (Registered Trade Mark) a film produced from wood pulp by the viscose process, which possess release properties in the untreated state. Generally, however, the inherent release properties of such films are not sufficient and must be improved by coating with release compositions, such as, the cured silicones mentioned hereinabove.

Such release sheets or surfaces, and methods for their preparation are well known. Typically, the paper or backing sheet is dipped into a bath of a silicone release agent, or coated on one or both faces with the release agent, and then cured. Such methods are described in U.S. Patent No. 3,503,782, incorporated herein by reference. Alternately, the release material may be knife or roller coated onto a sheet.

In any event, regardless what type release material is used, it is necessary only, that the surface 11 of the supporting or backing sheet 10 possess properties of good release with respect to pressure sensitive adhesive materials.

Alternately, the release surface can be the outer surface of the facing layer 10 of the laminate such that the laminate is rolled upon itself as described hereinafter with a reference to Figures 7 and 8. The release properties may be an inherent quality of the outer surface of the facing layer or a quality imparted through conventionally known finishing or coating techniques.

Disposed on top of the backing sheet 10 is a substantially uniformly distributed, discontinuous layer of a polysiloxane material designated generally as 12. This material is described in detail hereinafter and in Figure 2 is disposed on the surface of the backing sheet in the form of small droplets or beads.

As used herein, the terms "droplets" or "beads" means a relatively fine dispersion of small discrete quantities (resembling droplets or beads) of the interlayer formed on release surface 10. The nature of these small discrete quantities or droplets is discussed in detail hereinafter with respect to Figures 10 and 11.

The non-continuous layer 12 may be deposited on backing sheet 10 by numerous methods which are conventional in the art. The choice of technique may depend on the nature of the release layer and the nature of the facing layer, as well as the physical characteristics of the polysiloxane, e.g. viscosity, and liquid characteristics. Thus, for example, it is possible to spray the material on to the sheet or to use a padding roll, kiss roller or a rotogravure roll. Depending on the method of application, it is possible to control the deposition of the liquid material on the backing sheet, in terms of uniformity of application as well as discontinuity of the film. if the polysiloxane material is applied in the form of a solution or emulsion for purposes of the coating procedure used, it will be necessary, of course, to remove the diluent, i.e., solvent or dispersing medium. Such removal is conventionally effected by heating to evaporate the material to be removed.

Referring now to Figure 3, a layer of a pressure sensitive adhesive material is then coated on top of the backing sheet-polysiloxane combination of Figure 2 to form a laminate sometimes referred to hereinafter as a "first laminate". The coating of the pressure sensitive adhesive layer 14 may be accomplished by conventional methods, e.g., knifecoating, spraying, roller coating or gravure roll.

The pressure sensitive adhesive 14 may be one from a well known class of adhesive materials generally available in the art.

Typically, such an adhesive comprises a two component system, one component of which is a polymer or resin which is intrinsically tacky, such as a tacky elastomer, or has intermixed therewith, a resin imparting tackiness and a second component which is a tack controlling component to reduce the tack of the adhesive layer to the desired peel bond value. The second component also imparts cutting properties to the adhesive layer so that it will cut when the transferrable film, i.e., the facing layer is cut.

Also, as shown in Figure 5, it is important in the use of conventional pressure sensitive adhesive materials that the adhesive layer, 14, remain with the facing layer, and not with the release layer 10 upon stripping.

The second component is preferably a readily deformable material in order to allow the adhesive layer to make adequate contact with the receiving surface of the substrate which may be rough in texture. The tack controlling component is usually present in concentrations of from about 6 to 65 parts per 100 parts of the total tacky compound.

Intrinsically tacky polymers include polyacrylic or methacrylic esters and acids; polyvinyl ethers; co-polymers of vinyl ethers and the aforesaid acrylic compounds; polyisobutylene and polybutenes; natural rubber; synthetic polyisoprene; polyvinylesters; polychloroprene; polybutadiene and co-polymers of butadiene with styrene.

Tackifying resins include hydrocarbon

resins, terpene resins, such as, polybetapinene resin; resin derivatives, such as, hydrogenated resins and esters and liquid mixtures of polymeric styrene and homologues. Preferred materials are polyvinylbutylether; polyvinylethylether; polyvinylmethylether; polybutylacrylate or co-polymers of butylacrylate and methacrylate.

A detailed description of such materials is set forth in U.S. Patent No. 2,432,376, to which the present reader is referred for details.

Subsequent to the application of pressure sensitive adhesive layer 14, the laminate is subjected to a drying or curing step, such as, for example, heating, ultra violet irradiation, electron beam irradiation, or other methods which are conventionally used for such pressure sensitive adhesive materials. Understandably, the particular method used will be dependent upon the nature of the pressure sensitive adhesive material used; however, such methods are conventional in the art.

The pressure sensitive adhesive materials conventionally used are either soluble or dispersible in water or organic solvents. Also, materials have been developed which are themselves liquids, or possess relatively high solids content, but nevertheless can be coated or applied without dilution or emulsification. Also known are materials known as the "hot melt" type which are rendered coatable by heating. However, the particular type of pressure sensitive material used is not critical so long as it fulfills its function as a pressure sensitive adhesive and does not adversely affect the other desirable properties of the laminate.

Subsequent to the curing step, a facing layer 16 is married to the first laminate of Figure 3 to form the final laminate shown in Figure 4.

Facing layer 16 is generally a sheet material which can be decorative or protective in nature and can be wood, including wood veneer, metal, such as, metal foil, paper or a polymeric plastics film forming material, e.g., vinyl polymers such as, polyvinyl chloride, polyvinylidene chloride, copolymers of vinyl chloride and vinyl chloride and vinylidene chloride; polyolefins, e.g., polypropylene, polyethylene; polyesters; or knitted, woven or non-woven textile fabric; and the like known equivalent materials. Typically, the facing layer may have a decorative pattern embossed, printed, or otherwise imposed thereon. Alternately, the facing layer may be composed of two or more separate sublayers.

For example, it is possible to use a protective outer (otherwise 'top') layer which is substantially transparent sheet of a protective film, e.g., polyvinyl chloride, polyvinylidene chloride, copolymers of vinyl chloride and vinylidene chloride; polyesters, polypropylene, polyethylene, polyacrylates, polyurethanes, hard surfaced resins and a protected 'lower' sheet which may be composed of the same type materials as described hereinabove with respect to a single facing layer.

Generally, such a transparent layer can serve the function both of protecting the decorative pattern of the lower or bottom facing sheet, and in addition, can itself contribute to the over-all decorative appearance of the laminate, as by producing a shiny effect or high gloss.

Other types of decorative facing layers, such as flocked fabrics or films, or polymeric films, such as, polyester films having a thin deposit of metal thereon (metalized) or vinyl films coated with resin-pigment combinations in a decorative pattern can be used as the facing layer.

Figure 5 shows the method of utilization of the laminate in accordance with the present invention wherein components 12, 14, and 16, generally designated as 18, are separated from backing sheet 10.

On separation of the layers, an effective amount of the droplets of polysiloxane layer 12 is removed from release layer 10 and remains with pressure sensitive adhesive layer 14. Thus, the polysiloxane interlayer material 12 possesses a greater affinity for the pressure sensitive adhesive material of layer 14 than for the release surface 11 of sheet 10. Consequently, although a relatively small residue of the polysiloxane may remain on the removed release surface 11, the amount of the polysiloxane carried away from the release surface 11 by adhesive layer 14 is that amount which is effective to produce the desired reduction in "zero peel value" (as defined hereinafter) of the laminate 18.

It is understood, of course, that Figure 5 represents an approximate schematic view of the disposition of the droplets on the surface of the pressure sensitive adhesive layer, thus, when viewed microscopically, the pressure sensitive adhesive layer is not smooth but, possesses a surface having concave and convex portions. Consequently, the droplets may be disposed at the bottom of a concavity or on the top or side of a convex portion.

After stripping the release or backing layer 10 from layers 18, the combination of layers designated 18 may be applied to the desired substrate, e.g., furniture, walls or cabinet surfaces. By virtue of the unique properties of laminate 18 bestowed on it by the presence of droplets 12, it is possible to easily position layer 18 on to the substrate, to easily remove it and to reposition it if

necessary. Moreover, as noted hereinabove. if various portions of the pressure sensitive adhesive face of laminate 18 should touch one another, they are easily pulled apart without disturbing the uniformity of the pressure sensitive adhesive layer. Consequently, the usual tangles, wrinkles, creases, stretches, and like defects frequently encountered with pressure sensitive coated material of this type are avoided.

More particularly, the unexpected properties of the laminates embodying the present invention reside in the relative physical properties of the interlayer material composing droplets 12 to the pressure sensitive adhesive and the release material of backing sheet 10. It should be noted, in this regard, that once the laminate 18 is properly placed on the substrate, after a period of time, its adhesion to the substrate becomes essentially permanent and similar to that of conventional laminates of this type having the conventional pressure sensitive adhesive coated surfaces.

The method of forming laminates of the general type shown in Figure 4 are well known as illustrated by U.S. Patent Nos. 3,554,835, and 3,130,113, and the reader is referred to them for further details.

Referring now to Figure 6, a method for forming the laminate as described hereinabove comprises first coating a sheet of backing material 20 which suitably may be a kraft paper or other support sheet as defined hereinafter from roll 22 which turns in the direction indicated by arrow A with a suitable release material 24, such as, a silicone, or one of the other conventional materials used for this purpose.

The means for coating such material are well known, and as shown, a knife coater, 26, is utilized in the schematic. Thereafter, the coated sheet is passed through curing oven 28 which utilizes a conventional curing means, such as heat or ionizing radiation, to appropriately cure or set the release material. This produces a release surface 11 on sheet 30.

Release sheet 30 is then coated with the interlayer material from reservoir 32 utilizing gravure station 34.

As described hereinafter, this interlayer material possesses beneficial properties with respect to the release layer so that it forms beads or droplets thereon. The thus coated sheet is passed through a diluent removal step, e.g., a heating oven 35, to remove any diluent or solvent used for application of the interlayer. Ordinarily, the diluent removal step is carried out by heating at about 130—200°F although, of course, this depends on the diluent used.

It is noted, in this regard, that as used herein, the term "diluent" refers to the carrying medium used for the polysiloxane material. Thus, this includes not only solvents in which the polysiloxane is soluble, but also liquids in which the polysiloxane material may not be soluble but can be dispersed or emulsified.

Thereafter, the release sheet coated with the interlayer material is coated with a pressure sensitive adhesive 36 using a knife 38. Of course, various methods are known to the art for applying pressure sensitive adhesives and any of these conventional methods could be used.

After application of the pressure sensitive adhesive 36, the coated release sheet 30 is passed through oven 40 which utilizes conventional drying methods for pressure sensitive adhesive materials. Typically, temperatures in the range from about 190 to 280°F for about 5 to 20 seconds are used. For pressure sensitive adhesives which are in a prepolymer form, a curing treatment is generally required. Such treatments are conventional in the art and may utilize heat and/or ionizing radiation including both ultra violet curing as well as electron beam curing.

Typically, the pressure sensitive adhesive layer 14 has a composition as described above and generally has a thickness in the range from 0.1 to 7 mils (1 mil is 1/1000 inch); and preferably from 0.3 to 2 mils. Generally, it is coated in an amount from 0.5 to 8.0 mg./cm^2.

Thereafter, the thus coated and cured sheet designated as 42 is married to an appropriate decorative or protective facing layer 44 unrolled from roll 46. The two layers are married by passing through nip rollers 48 in a manner well known in the art. The pressure of nip rollers 48 generally ranges from 20—80 psi. Thereafter, the finished laminate is rolled onto roll 50 which revolves in the direction indicated by arrow B.

The overall thickness of the laminate is determined by the general end purpose for which it is to be used. Obviously, flexibility as well as weight would be factors which can be varied depending on this end purpose. Generally, however, in the sheet form of the present laminate intended for application by the consumer for general protective and decorating purposes the overall laminate thickness excluding the release layer is in the range from about 3 to 8 mils and preferably is from about 3.5 to 5.0 mils.

The foregoing described process is generally referred to in the art as an indirect type coating process. That is to say, it is a process for forming the laminate of the present invention wherein a release surface on a first sheet is coated with a

discontinuous, uniformly distributed, layer of a polysiloxane and then with a pressure sensitive adhesive to form a first laminate, the first laminate is subjected to conditions suitable to dry or cure the pressure sensitive adhesive, and the pressure sensitive adhesive side of the thus treated first laminate is married to one surface of a facing layer. When, either in use or in subsequent processing, the release layer is peeled from the facing layer, the pressure sensitive adhesive coating remains with the facing layer. Thus the layers which are to remain with the facing layer are indirectly coated thereon by first coating them on to the release surface and then transferring the layers by virtue of the peeling step.

The other type of coating process conventionally used in the art is known as the direct type process. This process will be described in detail with reference to Figure 8, hereinafter. However, generally, it refers to the process wherein a facing layer is coated with a layer of a pressure sensitive adhesive to form a first laminate, the first laminate is subjected to conditions suitable to cure or dry the pressure sensitive adhesive, the pressure sensitive adhesive side of the thus treated first laminate is coated with a discontinuous, uniformly distributed, layer of a polysiloxane and then married to a release surface. The ultimate product obtained, is, of course, the same in either case.

Referring now to Figure 7, an indirect coating process is shown wherein the final laminate does not possess a separate release layer. Rather, the final laminate is generally in roll form and is composed of a facing layer which possesses an outer surface and an inner surface, the outer surface being a release surface. A substantially continuous layer of a pressure sensitive adhesive material is adjacent to and contiguous with the inner surface of the facing layer and the discontinuous, uniformly distributed layer of the coatable polysiloxane is disposed between the pressure sensitive adhesive and the outer release surface of the facing layer.

In use, it is thus necessary only to unwind the facing layer from the roll whereupon it is ready for use since there is no separate release layer to peel. This form is particularly useful when the laminate is in the form of narrow tape and the like.

Such a roll may be formed utilizing the process depicted in Figure 7 wherein roll 100 which is a roll of backing sheet as described hereinabove having a release surface 102 is unwound in the direction shown by arrow C. At gravure station 104, the uniform, but discontinuos polysiloxane layer as described herein is applied to form a first laminate 106 which proceeds through drying oven 108. The dried first laminate is then coated with a pressure sensitive adhesive material 112 using coating knife 114 to form a second laminate 116. The second laminate is passed through drying or curing oven 118. Thereafter, the dried second laminate 120 is married to facing layer 122 which is unwound from roll 124 in the direction indicated by arrow D. The marrying operation is carried out by passing the combination of layers 120 and 122 through nip rollers 126.

It is noted that facing layer 122 possesses an inner surface 130 and another outer, surface 132. The outer surface possesses release properties. That is to say, outer surface 132 has been treated in such a manner so as to possess or is composed of a material which inherently possesses good release properties relative to the pressure sensitive adhesive material used.

Thereafter, married laminate 128 is passed through separator rollers 134 whereupon the release sheet 102 is separated from the final laminate 136. At the separation point designated as E, the pressure sensitive adhesive layer and the uniform, but discontinuous polysiloxane layer remain with the inner surface 130 of facing layer 122 to form final laminate 136.

Release sheet 102 is wound onto roll 138 which may be reused. Final laminate 136 is wound onto roll 140 in a direction indicated by arrow F. Thus, by virtue of the winding operation, the final laminate 136 is rolled upon itself such that the polysiloxane coated surface 142 is immediately adjacent to and contiguous with the outer release surface 132 of the facing layer. As rolled, the laminate is now ready for cutting, packaging and use by the consumer or final user.

It is also noted that it is possible, in such an indirect coating process wherein the final laminate is produced in roll form without a separate release layer, for release sheet 102 to be disposed in the form of an endless belt which would avoid rewinding it onto roll 138.

Figure 8 illustrates yet another method by which the laminate of the present invention can be produced in roll form without the presence of a separate release sheet in the final roll. Particularly, Figure 8 shows the direct method of coating referred to hereinabove. In this method, roll 200 of a facing layer having an outer surface 202 which possesses release properties and an inner surface 204 is unwound from roll 200 in the direction indicated by arrow G. The inner surface of facing layer 204 is coated with pressure sensitive adhesive material 206 using knife coater 208 to form a first laminate 210. First laminate 210 is passed to drying oven 212 and the dried first laminate 214 is coated with a discontinuous, but uniform film of

the polysiloxane described herein at gravure coating station 216 to form a second laminate 218. This second laminate 218 is passed through drying oven 220 to form final laminate 222 which is then rolled upon itself into roll 224 by winding in the direction indicated by arrow H. By virtue of winding in this direction, it is clear that the inner surface 204 of the facing layer which has thereon the coating of pressure sensitive adhesive and the discontinuous layer of the polysiloxane is rolled such that the polysiloxane layer is adjacent to the outer release surface 202 of the final laminate.

It is further clear that the process depicted in Figure 8 could be carried out such that subsequent to exiting oven 220, laminate 222 may be married to a separate release sheet in the manner shown in Figure 6 to form a final product having a separate release sheet.

In the case when the final product does not have a separate release sheet, it is possible to place it in stack form rather than in the form of a roll. Thus, referring to Figure 8, after exiting oven 220, the laminate 222 may be cut into separate and equally sized pieces or sheets and the separate sheets can be stacked one upon the other such that the polysiloxane layer of one sheet is immediately adjacent or next to the release surface of the facing layer of the next sheet in the stack. In use, therefore, it is only necessary to peel off the top sheet whereupon the next, uncovered sheet, presents itself for further use.

In the following discussion, reference is made only to the above embodiments of the present laminate wherein a separate release layer is present. It is clear, however, that the discussion also is applicable in all respects to other embodiments of the present laminate wherein a separate release layer is not present.

The laminate of the present invention described herein possess a number of advantageous properties as compared to known laminates generally used for the same type of purpose. The disadvantages of such prior laminates have been outlined hereinabove. More particularly, by virtue of the nature of the polysiloxane used as an interlayer material in the laminate of the present invention as well as its uniform, but discontinuous disposition on the pressure sensitive adhesive layer (once the release layer or surface has been removed) the present laminates overall, are usually easier to handle with respect to their application to a substrate than are prior known laminates.

Thus, generally, the present laminate (after separation of the release layer), upon being initially positioned on to the desired substrate, for example, a wall, can be easily removed without adverse affects. Should it be desired to reposition the laminate. This might occur, for example, in the case where the laminate, in its initial application to the substrate, was not straight, or possessed wrinkles, or bubbles. In such a case, the laminate may be easily removed by the applier without stretching the laminate or difficulty in pulling it from the substrate.

Moreover, should the laminate, during application, become folded upon itself so that different areas of the pressure sensitive adhesive surface touch one another, they, in turn can be easily pulled apart by the applier, and without adversely affecting the laminate for purposes of its reapplication.

Additionally, once the laminate has been applied to the satisfaction of the applier, it possesses sufficient adhesion to the substrate, so as to remain in the position applied. Also, over a period of time, for example, 20 minutes to an hour, the adhesion, or peel value as it is hereinafter defined, increases to a sufficiently high value to produce a permanent application on the substrate.

It is difficult to quantify the ease or difficulty with which the laminate can be initially applied or after such initial application, removed from the substrate. Thus, the ease of application of the laminate depends on the skill of the person applying the laminate as well as the nature of the particular substrate to which it is being applied. Many types of substrates, for example, walls, composed of painted wall board, painted cinder block or plastics, will be encountered by the typical user of this laminate, i.e., the consumer. As a result, depending on the particular nature of the end use, the ease of application and specific properties with respect to degree of adherence encountered with each of the different types of substrates will vary in an undeterminable manner.

However, for any given substrate, the person using the present laminates should encounter less difficulty in applying them as compared to use of the prior art laminates, i.e., a laminate without the specific interlayer required in the present invention.

Specifically, in addition to a facing layer and a pressure sensitive adhesive layer, the laminate of the present invention possesses means for decreasing the "zero peel value" (as defined hereinafter) of the facing layer-pressure sensitive adhesive layer combination composed of a discontinuous, uniformly distributed layer of a coatable polysiloxane adjacent to the pressure sensitive adhesive layer.

When a release surface or release layer is present in the laminate, the polysiloxane layer is disposed as an interlayer between

the pressure sensitive adhesive layer and the release surface or release layer.

Thus, by virtue of the presence of the polysiloxane interlayer of the present laminate, there is produced a substantially decreased initial adhesion of the laminate for a particular substrate as compared to that which would be encountered with a laminate not possessing the polysiloxane interlayer.

Additionally, however, the amount of the actual adhesion at the time of initial application of the laminate to the substrate is sufficient so as to assure that the laminate will remain adhered to the substrate and not separate by virtue of the laminate's own weight.

Moreover, as noted hereinabove, the adhesion of the laminate of the present invention to the substrate builds up within a reasonable amount of time so as to provide a permanent installation which is essentially equivalent to that obtained with a laminate without the interlayer of the present invention.

Yet a further advantage of the present invention is its unusual characteristic of regenerating relatively low zero peel values (hereinafter defined) after a substantial residence time on a substrate. That is to say, if the present laminate is applied to a given substrate and allowed to remain for a given period of time, e.g. eight hours, upon removal from the substrate (assuming such removal can be effected without multilating or destroying the substrate or laminate), it has been found that the laminate will exhibit a relatively low zero peel value. Thus, the properties of the present laminate with respect to its ease of initial application are not destroyed by virtue of such application, but continue to reappear should it be necessary to remove the laminate from the given substrate.

Another important feature of the laminate of the present invention is its excellent slip characteristics relative to the substrate. While this characteristic depends to some extent on the substrate involved, invariably, the lateral slip is substantially better with the present laminate than with a Control Laminate (defined hereinafter).

As used herein, the term "slip" means the ability of the laminate to slide on the substrate under light hand pressure. This property is quite difficult to quantify, although it is quite noticeable to the applier. Thus, for example, on applying the present laminate to a wall, by virtue of the excellent slip properties of the laminate, it can be actually placed against the wall, and, while being held against the wall with light hand pressure, slidably moved about the wall surface.

This property also manifests itself with respect to the ability of the laminate to slide across itself when one portion of the pressure sensitive surface touches another portion of the pressure sensitive surface.

In order to more quantitatively characterize the improved properties of the present laminate, the discussion following hereinafter will utilize a number of defined terms relating to the degree of adhesion of the laminate to a given substrate after a specified amount of time. Additionally, because, as noted above, many different types of substrates will be encountered, in an attempt to generally characterize the substrates, the defined values will be further limited to specific test substrate materials which are also described in detail hereinafter.

Additionally, in characterizing the properties of the present laminate, it is necessary to define such characteristics in terms of the difference between those same characteristics possessed by a Control Laminate. Such a Control Laminate consists of a laminte which is identical to the laminate of the present invention, except for the fact that it does not possess the polysiloxane interlayer of the product of the present invention between the pressure sensitive adhesive layer and the release layer.

Referring now to the polysiloxane material utilized as the interlayer, it must be devoid of certain properties which, if possessed, would make it unsuitable for use in the present laminate. That is to say, if it possessed such properties, the resulting laminate would not possess the advantages of the present laminate. For example, the interlayer material should possess a sufficient affinity for the pressure sensitive adhesive layer. If it does not possess a sufficient affinity for the pressure sensitive adhesive layer, then, as noted above, an effective amount of the interlayer material upon stripping of the release layer from the laminate, will not be available for use on that portion of the laminate which is actually applied to the substrate, i.e., the pressure sensitive adhesive coated layer.

In this respect, the polysiloxane utilized as the interlayer material in the embodiments of the present invention may be qualitatively characterized as a non-release material. That is to say, in the art, a "release material" is generally considered to be one which possesses relatively low affinity for a pressure sensitive adhesive and which easily separates from the pressure sensitive adhesive on peeling.

However, in the present invention, the polysiloxane used, preferentially remains with the pressure sensitive adhesive layer rather than the release surface where present. Consequently, in this context, the

polysiloxane possesses "non-release" properties.

Additionally, the polysiloxane cannot be miscible with the pressure sensitive adhesive material used. If it is, it will be completely absorbed or distributed into the pressure sensitive adhesive material of the laminate, and will not be available to engage the substrate surface when the laminate is applied to the substrate. Thus, it is important that the polysiloxane be present at the pressure sensitive adhesive substrate interface at the time of application.

In a similar manner, the polysiloxane possess certain other properties in order to make it suitable for use in the present laminate. Thus, it possesses the capacity of forming a non-continuous film on the surface to be coated. Generally, in practice, this film is seen as a series of small beads or minute droplets as it is disposed onto the surface. A material which is not capable of forming such a discontinuous film, would not produce a laminate having the desired properties.

As used herein, the term "uniform, but discontinuous", is meant to imply that the polysiloxane is uniformly distributed over the surface of the present sensitive adhesive, but that it is not a continuous film. As noted hereinabove, the polysiloxane is in the form of a multiplicity of small beads or droplets, thus forming a discontinuous film. However, it is apparent, that the polysiloxane cannot be uniformly distributed in the form of relatively large globules, which, while large, are spaced equal distances apart on the surface of the release sheet. Thus, a typical distribution of the polysiloxane on the pressure sensitive adhesive surface would have a multiplicity of such small droplets or beads within each square inch of surface area of the pressure sensitive adhesive.

A typical, but not necessarily critical type of distribution on the pressure sensitive adhesive layer is shown in Figure 9. This is a photograph taken of a laminate wherein a dye was included in the polysiloxane interlayer material prior to coating so that it could be visually distinguished from the pressure sensitive adhesive. The release layer, after preparation of the laminate in the manner disclosed herein, was then peeled from the facing layer-pressure sensitive adhesive combination, i.e. component 18 of Figure 5, and a photograph was taken of the pressure sensitive layer. The dark areas represent the colored interlayer material.

Figure 10 is a photograph similar to that of Figure 9; however, this is a view of the release surface of Figure 2 after the polysiloxane (containing a dye) was applied thereto by gravure roll. The arrow designated A in Figure 2 indicates the direction from which the photograph was taken. It is clear, from a comparison of Figures 9 and 10, that the actual configuration of the polysiloxane droplets on the pressure sensitive adhesive layer, after peeling from the release surface, corresponds essentially to the configuration of the droplets at the time of application of the polysiloxane to the release surface, e.g., at gravure station 34 of Figure 6. The additional matter visible in Figure 10 derives from printing on the reverse side of the release sheet 10, and is not relevant to a comparison of the configurations of the polysiloxane droplets in Figures 9 and 10.

It is further apparent that the polysiloxane material could be distributed in a variety of patterns resulting in somewhat less than complete coverage of the droplets on the pressure sensitive adhesive layer. For example, the polysiloxane could be distributed in the form of a plurality of very thin parallel or crisscross ribbons or lines on the pressure sensitive adhesive surface. Such a configuration would, of course, produce a uniform and discontinuous film and the properties of the resulting laminate would differ only in degree from the preferred form of the configuration described therein, i.e., a uniform distribution of beads or droplets.

Also important is the capability of the polysiloxane material to be coated onto the desired surface. This characteristic is referred to herein as the property of being "coatable" which is intended to have that meaning conventionally given to it in the laminating art, with reference to the coating of films, whether continuous or discontinuous, onto surfaces during the preparation of such laminates. That is to say, the material must be in a physical form suitable for allowing it to be spread or sprayed onto a surface in a relatively thin continuous or discontinuous film. Thus, for example, in order for a pressure sensitive adhesive material to be used in such a laminate, it must be either coatable, in and of itself, or be capable of being put into a form whereby it can be coated.

Consequently, the property of being coatable, as that term is used herein, does not necessarily mean, that the polysiloxane material, in and of itself, must be of such a viscosity (or molecular weight), that it can be coated without further dilution or emulsification. It is sufficient that the material be susceptible to such dilution or emulsification, or other treatment, so as to allow it to be applied in a uniform, but discontinuous film onto the desired surface. Typically, for example, such material can

be formed into an emulsion (generally an aqueous emulsion) or dissolved in an appropriate solvent.

If the material cannot be coated onto a surface, then, as is apparent, it cannot be used to make the laminate of the present invention.

Understandably, the molecular weight, or the viscosity of the interlayer material is a factor in determining whether or not the material will be coatable in accordance with the above definition. Considering the nature of the specific polysiloxane materials defined hereinbelow, it is clearly within the skill of the art worker to adjust the molecular weight, and/or viscosity of the material so that it is coatable.

With respect to the characterizing parameters used herein, the following constitute defined terms:

1. Peel Value

Die-cut 1"x6" samples of the laminate are mounted on 2"x6" surfaces of "Stainless Steel", "SBR" or "Acrylic" surfaces, as defined hereinafter. The specimens of the laminate are mounted by first removing the backing release sheet and placing the adhesive coated component in the center of the test panel. The specimen is smoothed onto the panel lightly with the hand leaving the last inch of the specimen free from the panel. Thereafter, a strip of the backing paper that was removed is placed under the last free inch in order to provide means for lifting the specimen from the test panel.

The specimen is then rolled using a 4-1/2 pound rubber hand roller for 15 seconds in each direction employing no additional hand pressure, i.e., the total pressure is supplied by the weight of the roll itself.

The sample is then allowed to remain at room temperature for the specified period of time. In the case of the peel value at zero time, the specimen is removed from the panel with 10—15 seconds actual elapsed time from the time of mounting.

The test panel is mounted into the lower jaw of an Instron machine Model No. TM-2360-011, and the free end of the strip of backing paper is placed in the upper jaw. The sample is then peeled back on itself at an angle of 180° for a distance of 2.48 inches and the average peel adhesion strength is recorded in grams per inch of width. This value represents the peel value for the indicated time period.

This procedure was used to determine all peel values referred to herein. Preferred values are less than 600 grams on the stainless steel surface, and less than 500 grams on the acrylic and SBR surfaces.

2. Stainless Steel Surface

The stainless steel surface is a sample of stainless steel conforming to QQ-S-766, Class 302 or 304 (AISI 302 or 304) stainless steel having a bright annealed finish. The surface roughness height is 2.0 micro inches ±1.0 micro inches arithmatical average deviation from the mean line, as obtained from the Pressure Sensitive Tape Council, 1201 Waukegan Road, Glenview, Illinois 60025.

3. "Acrylic" Surface

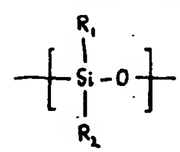
A 3/8" standard wallboard surface painted with two coats (with a roller) of an interior white acrylic based latex paint (DuPont) Lucite (Registered Trade Mark) 2360 interior latex paint).

4. "SBR" Surface

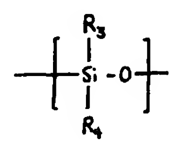
A 3/8" standard wallboard surface painted with two coats (with a roller) of styrene-butadiene rubber based paint (Sherwin Williams Latex Interior Edgewater Blue).

5. All viscosities were measured at about 25°C (room temperature) using a Brookfield Synchro-Lectric, Model LVT viscometer and are reported in centiposes (cps).

Referring now in greater detail to the polysiloxane, the material which we have found to possess all of the above noted properties, and to produce the desired advantageous properties in the laminate obtained are coatable polysiloxanes consisting of monomeric units having structures (I) and (II) as follows:

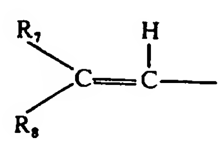
(I) 

and

(II) 

wherein

R_1 is:

(i) phenyl;
(ii) methyl;
(iii) tolyl;
(iv) 

wherein R_7 and R_8 are the same or different and are hydrogen, methyl, or ethyl; or

(v) polyoxalkylene having the structural formula

$$-R_5(OC_2H_4)_n(OC_3H_6)_mOR_6$$

wherein R_5 is an alkylene group having at least two carbon atoms, R_6 is a monovalent hydrocarbon group having from 1 to 10 carbon atoms, n and m are integers the sum of which is such that the oxyalkylene block

$$R_6O(C_3H_6O)_m(C_2H_4O)n$$

has a molecular weight of at least 1500 and from 15 to 60 weight percent of the oxyalkylene units are oxyethylene units, and wherein the oxyalkylene block constitutes from 85 to 30 weight percent of the polysiloxane polymer;

R_2 is methyl, ethyl, or phenyl; and

R_3 and R_4 are the same or different and are methyl or ethyl;

with the proviso that when R_1 is group (i), (ii), (iii) or (iv), the prime mole percent of structure (I) is from about 0.5 to about 50 and the prime mole percent of structure (II) is from about 99.5 to about 50, and when R_1 is group (v), there are at least three units having structure (I) and at least 40 units having structure (II).

Preferred are those polysiloxanes wherein R_1 is phenyl, R_2 is phenyl or methyl, and R_3 and R_4 are methyl. Such polysiloxanes are particularly desirable when the prime mole percent of (I), x, is from 0.5 to 30 and the prime mole percent of (II) y is from 99.5 to 70.0. Generally, when R_1 is phenyl and R_2, R_3, and R_4 are methyl, in accordance with the above, the preferred polysiloxane has a number average molecular weight from 25,000 to 250,000, although, here again, the prime factor in determining molecular weight is the ability to coat or to render the polysiloxane coatable. Particularly, preferred is a polysiloxane wherein R_1 is phenyl, and x is about 4.5, and the number average molecular weight is about 70,000.

Also desirable are polysiloxanes having the above structural formula wherein R_1 is methyl and x equals y. Generally, such polysiloxanes have a viscosity in the range from 60×10^3 to 20×10^6 cps.

Another preferred polysiloxane within the scope of the above formula is that wherein R_1 is a vinyl group and x is from 40 to 60, and y is from 60 to 40, and the number average molecular weight is in the range from 5×10^5 to 1×10^6.

As used herein, the term "prime mole percent" is the number ratio of the x type to y type siloxane units, multiplied by 100.

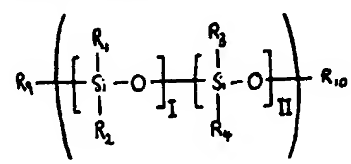
Such polysiloxane as well as methods for their production are conventional and are described in detail in U.S. Patent No. 2,560,498, to which the reader is referred.

Another class of desirable polysiloxanes are those wherein R_1 is the polyoxalkylene block described hereinabove. Methods for preparing this class of material is described in U.S. Patents 3,505,377 and U.S. Reissue Patent No. 27,541, to both of which the reader is referred.

Particularly preferred in this class of polysiloxanes is a hydrolytically stable silicone surfactant composition containing a dimethylsiloxane - oxyalkylene block copolymer wherein the oxyalkylene block of the copolymer contains oxyethylene and oxypropylene units and R_2, R_3 and R_4 as described hereinabove are methyl and which possess a viscosity at room temperature of about 2250 cps. (measured with a number 4 spindle at 30 r.p.m.).

It is noted that inasmuch as the siloxane polymer utilized must be coatable, they are, generally, not cross-linked, nor do they cross-link over a period of time under normal storage conditions or in the absence of cross-linking agents.

Typically, the polysiloxanes which can be used in the present invention have the structural formula:



wherein R_1, R_2, R_3, R_4 and the prime mole percent or number of structural units designated I and II are as defined above. R_9 and R_{10} are polymer chain terminal groups. Due to the relatively long length of the polymer chains, the particular groups constituting R_9 and R_{10} are present in trace amounts. Consequently, the effect of such groups, even if they are chemically reactive, i.e., can react with certain of the other chemical entities in the polymer, is minimal, and, as a practical matter, undetectable. Thus, while it is preferred that R_9 and R_{10} are hydrogen or saturated lower alkyl, e.g., having 1 to 10 carbon atoms, the particular chemical nature of such terminal groups is not critical so long, of course, as the groups do not adversely effect the desired properties of the polysiloxane.

The value of subscript "n" determines the molecular weight of the polymer and, as discussed hereinabove, is such that the polysiloxane is coatable.

The polysiloxane materials utilized in preparing the preferred laminates of the present invention may be deposited or

applied onto the release surface using a variety of techniques well known and conventional in the art. Thus, for example, the polysiloxane, whether it is used as is, or diluted either in a solvent or an aqueous emulsion may be applied using a gravure roll, knife overroll, a reverse roll coating technique, the so-called flexographic printing technique, or a controlled spray. It is thus within the skill of the art to use any of these techniques to apply the polysiloxane material and to regulate the parameters affecting the deposition, e.g., concentration or roll speed so as to deposit a uniform discontinuous film in accordance with the description hereinabove.

Insofar as the actual physical form of the polysiloxane material with respect to the deposition technique is concerned, any type of conventional organic solvent e.g., aliphatic and aromatic organic solvents can be used. The controlling factor in the selection of such a solvent is merely that it be one which is commercially available and does not have an adverse influence on either the economics of the process or product and of course, does not adversely affect the product itself.

Alternatively, the polysiloxanes may be incorporated into an aqueous emulsion using conventionally known emulsifying agents and conventional emulsifying techniques. Here again, such techniques are well known to the skilled artisan in this technical field.

It is further possible, depending on the viscosity of the undiluted polysiloxane material, to use it as is, without a diluent.

The amount of the deposit can vary over a wide range and depends on the specific polysiloxane which is used as well as the technique used for coating and other parameters which would be characteristic of the specific process being used. However, conventional art techniques would be used to adjust and to optimize these parameters in order to optimize the product properties.

For example, if a rotogravure deposition technique is used with a solution of the polysiloxane in an appropriate organic solvent, the concentration of the solution would vary depending on the specific type of rotogravure roll used, i.e., the number of lines per inch, and the design on the rotogravure roll, e.g., straight line or pyrimidal.

We have found, generally, that such solutions will most preferably have a concentration from about 0.125 to 15% by weight in the given solvent. Within this concentration range, using rotogravure or spray techniques, it is possible to deposit from about 0.002 to about 1.0 gram per square meter on a dry weight basis of the polysiloxane and this generally will lead to a product having properties within an optimal range.

In any event, the specific manner of deposition should be regulated so as to produce a substantial decrease in the zero peel value of the product as compared to a control laminate and to provide for a twenty minute peel value of at least about 100 grams. Preferably, the reduction in the zero peel value as compared to the zero peel value of the control laminate is in the range of at least greater than about 25%. It is possible, of course, that for a specific purpose, the skilled artisan might desire to decrease the percent reduction in the zero peel as compared to the control laminate.

All of the above mentioned deposition techniques lend themselves to the formation of a uniform but discontinuous film of the polysiloxane material onto the release surface or the pressure sensitive adhesive surface depending on whether a direct or indirect coating process is used. As noted, a typical illustration of such a uniform but discontinuous deposit is shown in Figures 9 and 10.

The following examples illustrate the present invention:

EXAMPLE 1

A release sheet was prepared from kraft paper (42 pounds per ream) by coating it with a conventional silicone release finish, for example, Dow Corning Syloff 23 with DC 23 A catalyst, the amount of coating being about 0.5 pounds per ream. The paper was coated on the machine finished face. The coating was carried out using an 80 line quadrangular gravure coating roll.

The solids content of the silicone release material in Tolusol 50 (a 1:1 mix of toluene and heptane) was 3.8%. After coating, the coated paper was subjected to drying and curing conditions in an oven at about 350° to 400°F for about one minute.

The kraft paper used, in the usual commercial embodiments, generally carries printed information, e.g., application instructions, suggested use or measuring scales to facilitate cutting, on the non-release side.

A solution of 3% to 10% by weight of a phenyl methyl dimethylpolysiloxane containing about 4.5 prime mole percent of phenylmethylsiloxane groups and having a viscosity of 18,000 cps (number 4 spindle at 30 rpm) was prepared in Tolusol 50 solvent. It was applied to the above prepared release paper using a 165 line quadrangular gravure roll. The thus coated release sheet was dried at a temperature of about 160 to 180°F for about 15 to 30 seconds using heat circulating ovens. The deposit of the

polysiloxane material was in the form of a uniformly distributed discontinuous film similar to that illustrated in Figure 10 hereof. The dried deposit of the polysiloxane on the release sheet was thus about 0.17 to 0.5 grams/m^2.

A pressure sensitive adhesive was then coated onto the thus treated release layer with the polysiloxane thereon. For this purpose, an aqueous emulsion of an acrylic-vinyl acetate copolymeric pressure sensitive adhesive having a solids content of about 50.0% by weight, a viscosity of 481 cps (#3 spindle at 60 rpm) and a plasticity of 1.7 mm (hereinafter referred to as "P.S.A. 1" was used. The adhesive was applied by reverse roll coating . Alternatively, a 55 line quadrangular gravure roll can be used. The dry deposit of the pressure sensitive adhesive ranged from about 1 to 2 milligrams per square centimeter.

Thereafter, the sheet coated with the pressure sensitive adhesive was dried at about 240°F for about 5—10 seconds to remove the water from the emulsion.

Finally, a polyvinyl chloride film having a thickness of about 3.5 mils was married to the thus coated release sheet by passing the combination through a nip at a pressure of about 30 psi. The final product was rolled into a suitable package for subsequent cutting and packaging.

Alternately, other commercial pressure sensitive adhesives may be used. For example, an acrylic-vinyl acetate copolymer (water base) having a solids content of about 53.0, a viscosity of 837 cps (#3 spindle at 60 rpm) and a plasticity of 2.70 mm (hereinafter referred to as "P.S.A. 2"), an all butyl polyacrylate based pressure sensitive adhesive, (water base) having a solids content of 57, a viscosity of 302 cps (#3 spindle at 60 rpm) and a plasticity of 1.64 mm (hereinafter referred to as "P.S.A. 3"), or an organic solvent base pressure sensitive adhesive, such as, an acrylic-vinyl acetate polymer having a solids content of about 32.3, a viscosity of 491 cps. (#2 spindle at 30 rpm) and a plasticity of 1.53 mm. (hereinafter referred to as P.S.A. 4) may be used. These are typical of the commercially available pressure sensitive adhesives which are conventionally used for preparation of these types of laminates.

Depending on the specific pressure sensitive adhesive and type of release surface used, the preferred method of deposition, i.e., concentration of the polysiloxane in the diluent can vary. For example, with the P.S.A. 1 and P.S.A. 3, the preferred concentration is from about 8 to 10% by weight, whereas with P.S.A. 2, a concentration of about 3 to 5% by weight is preferred.

In addition to the above described acrylic based pressure sensitive adhesive materials, the laminate of the present invention can be prepared using other conventional pressure sensitive adhesive systems such as, those composed of styrene-butadiene copolymer, a highly stabilized ester resin and an anti-oxidant. A typical formulation of such an adhesive system can be prepared by mixing 100 parts of styrene-butadiene copolymer having 23.5% bound styrene (Ameripol 1011 manufactured by B. F. Goodrich) with 75 parts of a highly stabilized ester resin (Foral 85 manufactured by Hercules, Inc.) and two parts of an anti-oxidant, such as, for example 2, 2' - methylene - bis(4 - methyl 6-t-butyl phenol), (Antioxidant #2246 manufactured by American Cyanamid).

EXAMPLE 2

A series of laminates in accordance with the present invention were prepared using the process conditions and components and procedures set forth in Example 1. However, a series of three different polysiloxanes were used, and were applied in solution concentrations ranging from 5 to 15 weight percent. Additionally, two different pressure sensitive adhesives were used. Thus, each particular polysiloxane material and each concentration level was utilized to prepare a laminate sample with each one of the two different pressure sensitive adhesives.

Thereafter, the zero minute and twenty minute peel values were determined. Also determined were the peel values of the samples after they had aged for 16 hours and 7 days, respectively, although the 7 day peel value was determined only on the stainless steel surface. The results of these analyses are set forth in Table 1 hereof.

The pressure sensitive adhesives used were P.S.A. 1, and P.S.A. 4.

The polysiloxanes used were the phenylmethyldimethyl polysiloxane of Example 1, hereinafter referred to as interlayer A, a dimethylpolysiloxane having a viscosity of about 60,000 cps (referred to hereinafter as interlayer B), and a dimethylsiloxane-oxyalkylene block copolymer containing oxyethylene and oxypropylene units and having a viscosity of about 2250 (referred to hereinafter as interlayer C).

The application of the solutions of the polysiloxanes was performed using a 165 line quadrangular cell rotogravure roll.

Additionally, two control samples were prepared using each of the pressure sensitive adhesives. These control samples were prepared in an identical manner to each of the other samples except that the polysiloxane interlayer was not present.

The results obtained are set forth in Table 1.

TABLE 1

Sample/ Conc.	Interlayer/ PSA	PEEL VALUE (grams) AFTER ROOM TEMPERATURE AGEING									
		ZERO MINUTES			20 MINUTES			16 HOURS			7 DAY
		SS	SBR	ACR.	SS	SBR	ACR.	SS	SBR	ACR.	SS
A	P.S.A. 4 Control	572	430	569	855	602	799	1176	934	836	1457
B	P.S.A. 1 Control	509	407	604	595	604	950	830	1071	1116	875
C/5%	C /P.S.A. 1	157	232	308	339	340	462	510	605	902	775
D/10%	C /P.S.A. 1	159	211	265	321	284	450	516	475	730	725
E/15%	C /P.S.A. 1	62	192	221	426	246	350	484	442	544	645
F/5%	C /P.S.A. 4	154	197	277	329	248	460	699	497	763	1025
G/10%	C /P.S.A. 4	191	259	354	404	341	548	749	602	791	915
H/15%	C /P.S.A. 4	62	170	271	172	204	582	445	362	929	925
I/5%	A /P.S.A. 1	222	306	378	397	450	625	610	802	949	725
J/10%	A /P.S.A. 1	171	337	354	345	445	520	542	750	982	790
K/15%	A /P.S.A. 1	101	283	255	265	430	408	444	787	768	875
L/5%	A /P.S.A. 4	232	363	405	530	534	715	841	809	970	1300
M/10%	A /P.S.A. 4	131	302	396	649	473	730	1022	832	1214	1435
N/15%	A /P.S.A. 4	214	228	254	585	396	510	1018	773	1005	1625
O/5%	B /P.S.A. 1	261	361	432	402	472	649	613	725	967	800
P/10%	B /P.S.A. 1	209	378	390	336	544	562	539	1040	1000	690
Q/15%	B /P.S.A. 1	196	284	406	326	378	572	523	642	1007	625
R/5%	B /P.S.A. 4	469	441	526	688	613	708	1110	961	1170	1400
S/10%	B /P.S.A. 4	257	348	471	544	514	707	1011	912	1185	
T/15%	B /P.S.A. 4	241	274	370	522	402	475	1033	854	1030	1220

NOTE: In this Table only, one reading was taken for each Sample except for the Zero Minute Value in which the Average of two Readings is Tabulated.

As can be seen from the data in Table 1, by controlling the amount of the polysiloxane deposited, the desired decrease in the zero peel value can be obtained.

As further shown from the 20 minute peel value and the extended application peel values, i.e., 16 hours and 7 days, a significant build up in the peel value is effected as the peel values approach those of the controls.

For purposes of subjective evaluation, in separate tests, each of the samples obtained was hand tested for ease of application of a 6 foot long 18 inch wide sample onto a wall having each of the above defined sufaces. In each case, those samples in accordance with the present invention exhibited remarkably easier application properties to the wall then did the corresponding control samples. Thus, samples C through T could be easily applied to the wall, easily removed therefrom for repositioning or straightening, did not exhibit as many wrinkles or air bubbles, and the wrinkles and air holes that were present were easily smoothed out or removed, in contrast to the control samples which presented much more difficulty with respect to these subjective parameters.

In the same subjective manner, the samples were checked for "slip" as defined hereinable and the capacity to be pulled apart when two portions of the pressure sensitive adhesive surface touch one another. For this latter characteristic, a portion of the sample was folded upon itself and pressed with strong hand pressure and then peeled apart. In each instance, the samples prepared in accordance with the present invention were easily peeled with no noticeable pulling of the adhesive layer.

Moreover, when each of the control samples were folded adhesive-side to adhesive-side, and pressed together under strong hand pressure, it was difficult, if not impossible, to peel the two sides from one another without significant stretching of the vinyl and distortion of the pressure sensitive adhesive surface.

EXAMPLE 3

A series of experiments was carried out to illustrate the effect of different methods of application of the polysiloxane material. In these tests, the procedures set forth in Example 1 were followed, except for the variables defined hereinbelow. The pressure sensitive adhesive material used was P.S.A. 1, and the polysiloxane was interlayer A.

Various concentrations of the polysiloxane in Tolusol 50 were applied using a 165 line quadrangular gravure roll at various application pressures.

In order to effect zero pressure of the roll, the pressure sensitive adhesive material was directly coated onto the vinyl film and then the various concentration solutions of the polysiloxane were directly coated onto the surface of the pressure sensitive adhesive using a 165 line gravure roll. The product was then dried and was not subjected to a laminating nip. However, a release sheet was applied to the surface by hand in order to protect the surface from contamination.

Also, in order to effect zero pressure, a series of polyvinyl chloride fiber samples having the pressure sensitive adhesive material coated thereon in the conventional manner were sprayed using solutions of the polysiloxane material which varied in concentration. The spraying was carried out using a fifty pound air pressure, a #36 nozzle, with one pass at 14 inches from the surface of the adhesive.

Additionally, several solutions of differing concentrations of the polysiloxane were applied to the release sheet with a 165 line quadrangular gravure roll, and then the film was laminated to the thus coated and dried release sheet using nip pressures of 10, 20, 40, and 80 pounds per square inch.

The peel values at zero time, at 5, 10, and 60 minutes were determined.

The results of the test with the 5% solution of the polysiloxane are shown in Figure 11. As can be seen from this Figure, for those samples wherein the polysiloxane was used, significant and substantial decreases in the initial peel values were obtained as compared to that of the control sample which was prepared in the conventional manner using a fifty pound nip pressure for the lamination.

Figure 12 shows the change in peel value with time for solutions of the polysiloxane having varying concentrations when such solutions were sprayed onto the pressure sensitive adhesive.

In each case, it is seen that by virtue of the use of the polysiloxane interlayer of the present invention, significant decreases in the peel values at zero time and in the range from 20 to 30 minutes can be obtained. Moreover, these peel values build up in time to provide a permanent adhesion of the laminate to the particular substrate.

This data further illustrates the manner in which the process parameters can be varied to achieve different degrees of change in the initial peel value from the control in accordance with the desire of the skilled artisan and the specific end use intended for the laminate.

EXAMPLE 4

A series of samples were prepared using the procedures set forth in Example 1

hereinabove and utilizing P.S.A. 1 and interlayer A as the polysiloxane material.

Various concentrations of the polysiloxane in Tolusol 50 were used and were applied to the release sheet using 80, 120, and 165 line quadrangular cell gravure rolls.

Depending on the concentration of the solution and the size cells of the gravure roll, the amount of deposit and zero peel value varied. It is noted that the 80 line roll possesses larger cells than the 165 line roll. In fact, in terms of volumetric capacity, the 80 line roll deposits 2.6 times as much volume per cell as compared to the 165 line roll and the 120 line roll deposits 1.6 times as much volume per cell as the 165 line roll.

The peel values of the various samples produced after various ageing times starting with zero time as defined herein were measured.

Figures 11, 12, and 13, show the variation in peel value with time for samples prepared using varying concentrations of the polysiloxane deposited with gravure rolls having 165 lines per inch, 120 lines per inch, and 80 lines per inch, respectively. As shown in these Figures, in each and every case, the same general trend with respect to decreasing initial peel value is observed as the amount of polysiloxane material is increased either by virtue of the concentration used with a given gravure roll or by virtue of using a larger cell gravure roll.

Figure 14 shows the change in peel value with time for a specific concentration solution of the polysiloxane (10% by weight) with changing cell volume in the gravure roll. Thus, as can be seen, a significant decrease in the zero peel values from that of the control are realized and also, with increasing volume of the gravure roll cells, a general decrease in the peel value for any given time period is observed.

The same general trend is seen for other concentrations of the polysiloxane material.

EXAMPLE 5

The laminate as prepared in Example 1 in accordance with the present invention using P.S.A. 1, was subjected to a series of peel tests at various times in conjunction with a control. Particularly, samples of each of the laminates were adhered to an acrylic painted test substrate for periods of zero minutes, 20 minutes, 1 hour, 3 hours, 5 hours, and 16 hours. The peel value at each of these periods of time was then measured. Additionally, after having the peel value measured at the specified time, each sample was then readhered to the substrate and tests for zero peel and 20 minutes peel. These latter two values are referred to in this example as "repeat zero peel", and "repeat 20 minute peel". Thus for example, considering the sample which was allowed to remain on the substrate for one hour, after it was removed and the one hour peel value determined, the sample was then reapplied to the acrylic substrate for determination of its repeat zero peel, and repeat 20 minute peel. The results from these tests are tabulated in Table 2.

TABLE 2

		CONTROL	LAMINATE OF PRESENT INVENTION
		Peel Value	Peel Value
Zero Minutes	0	463	251
	Repeat 0	373	192
	20 Min.	587	304
20 Minutes	20 Min.	629	394
	Repeat 0	429	221
	Repeat 20 Min.	580	333

TABLE 2 (cont.)

		CONTROL	LAMINATE OF PRESENT INVENTION
One Hour	1 Hour	729	449
	Repeat 0	478	255
	Repeat 20 Minutes	670	379
Three Hours	3 Hours	801	574
	Repeat 0	467	287
	Repeat 20 Minutes	665	372
Five Hours	5 Hours	777	585
	Repeat 0	510	284
	Repeat 20 Minutes	653	407
Sixteen Hours	16 Hours	993	627
	Repeat 0	587	334
	Repeat 20 Minutes	740	398

As shown in Table 2, one of the very desirable characteristics of the laminate in accordance with the present invention is that even after a significant amount of time, the peel value is not so high as to adversely affect the substrate should it be desired to remove the laminate from the substrate, although the peel value does build up to a level which is more than adequate for a permanent installation. Moreover, upon such removal, the repeat zero peel which the laminate exhibits is relatively low. Thus, upon removal from the substrate even after the extended period of time, i.e., 16 hours in this case, the laminate exhibits peel values which are sufficiently low so as to facilitate the reapplication of the laminate to a substrate with essentially the same ease with which it was initially secured to the substrate.

EXAMPLE 6

Siliconized #42 machine finished paper (designated herein as MF #42) and siliconized kraft paper having a polyethylene coating were gravure coated using a 165 line quadrangular cell gravure roll and varying concentrations of interlayer A as used in Example 1 in Tolusol 50 solvent. The samples were subsequently dried in an oven. Half of the samples were coated with 0.35 ounces per square yard (dry weight) of P.S.A. 1 pressure sensitive adhesive and the remaining half were coated with 0.33 ounces per square yard (dry weight) of P.S.A. 4 adhesive. Control samples wherein interlayer A was not used were also produced.

The adhesive coating was dried in an oven and a 3.5 mil polyvinyl chloride film was married onto the thus dried adhesive at the oven exit and passed through a nip roller at a 40 pounds per square inch pressure.

A series of the Control samples were used for direct coating of the interlayer material onto the adhesive surface. For this purpose, the release sheet was removed from the Control sample (controls having both types of pressure sensitive adhesives

utilized for this) and interlayer A was applied using a 165 line roll directly onto the surface of the adhesive. The volatiles were driven off in an oven and the release sheet was relaminated to the directly coated pressure sensitive adhesive-vinyl combination by passing through a 40 psi nip roll.

For those samples which were directly coated, tests wherein the interlayer material was dyed showed that essentially none of the interlayer material was removed upon stripping of the release sheet. Thus, in the indirect coating process, wherein the interlayer material is coated onto the release layer, upon stripping the release layer from the remainder of the laminate, a very small amount of the dyed interlayer material is observed to adhere to the release surface.

In contrast, on using the direct application approach as described herein above, and on subsequent peeling of the release layer, relatively little, if any residue of the interlayer material can be seen on the release surface.

As a result, it can be assumed that 100% of the polysiloxane remains on the pressure sensitive adhesive. Consequently, the actual amount of interlayer material on the adhesive surface can be calculated from a knowledge of the concentration of the original application solution of the interlayer material, the volume of the cells of the rotogravure roll, and the specific gravities of the solutions used.

On each of the samples thus prepared, peel values at zero time, 5 minutes, and 20 minutes were determined. A summary of the results obtained with these tests is set forth in Table 3.

TABLE 3

Adhesive	Release Sheet	Concentration of Interlayer Material % Weight	Amount of Interlayer Deposited g/m^2	Method of Applying Interlayer	% Reduction in Zero Peel From Control	Amount of Interlayer Deposit Required to Obtain 25% Reduction in Zero Peel from Control (g/m^2)
P.S.A. 1	MF #42	0.5	0.029	Indirect	25.0	0.0500
P.S.A. 1	MF #42	0.125	0.0073	Direct	36.0	0.0035
P.S.A. 1	Polyethylene Coated	1.0	0.058	Indirect	31.7	0.0360
P.S.A. 1	Polyethylene Coated	0.125	0.0073	Direct	26.0	0.0023
P.S.A. 4	MF #42	1.0	0.058	Indirect	23.6	0.0710
P.S.A. 4	MF #42	0.125	0.0073	Direct	22.0	0.0120
P.S.A. 4	Polyethylene Coated	0.5	0.029	Indirect	37.0	0.0240
P.S.A. 4	Polyethylene Coated	0.25	0.016	Direct	36.0	0.0095

The data in Table 3 illustrates the variation in the percent reduction in zero peel as compared with the control with respect to the use of different adhesives as well as different types of release sheets and methods of application. However, in each and every case, a significant reduction in the zero peel value was obtained when the interlayer in accordance with the present invention was used.

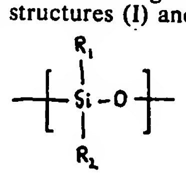
This data also indicates that the direct method of application appears to be somewhat more efficient than the indirect method. However, at the present time, the direct method is not as commercially preferred. This is primarily due to the difficulty in carrying the facing layer through a series of processing steps. Thus, in the indirect method it is the release sheet which is carried through the various process steps and the facing layer, which generally tends to have less dimensional stability than the release sheet, only enters at the very last step in the process.

The last column in Table 3 sets forth the amount of polysiloxane deposit required for each pressure sensitive adhesive-release sheet combination and method to give a 25 percent reduction in peel value as compared to the Control. These values were determined by graphically plotting the variation in percent reduction of the peel value with the amount of polysiloxane deposited and tabulating the amount of deposit at the 25 percent reduction point. It is thus apparent that these values are independent of the concentration of the polysiloxane solution.

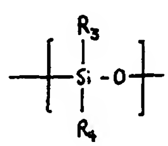
WHAT WE CLAIM IS:—

1. A laminate which comprises a discontinuous, uniformly distributed, polysiloxane layer on a substantially continuous layer of pressure sensitive adhesive on one surface of a facing layer, the polysiloxane consisting of monomeric units having structures (I) and (II)

(I)



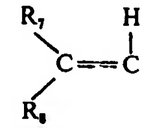
(II)



wherein

R_1 is

(i) phenyl;
(ii) methyl;
(iii) tolyl;
(iv)



wherein R_7 and R_8 are the same or different and are hydrogen, methyl, or ethyl; or

(v) polyoxalkylene having the structural formula

$$-R_5(OC_2H_4)_n(OC_3H_6)_mOR_6$$

wherein R_5 is an alkylene group having at least two carbon atoms, R_6 is a monovalent hydrocarbon group having from 1 to 10 carbon atoms, n and m are integers the sum of which is such that the oxyalkylene block

$$R_6O(C_3H_6O)_m(C_2H_4O)n$$

has a molecular weight of at least 1500 and from 15 to 60 weight percent of the oxyalkylene units are oxyethylene units, and wherein the oxyalkylene block constitutes from 85 to 30 weight percent of the polysiloxane polymer;

R_2 is methyl, ethyl, or phenyl; and

R_3 and R_4 are the same or different and are methyl or ethyl;

with the proviso that when R_1 is group (i), (ii), (iii) or (iv), the prime mole percent of structure (I) is from 0.5 to 50 and the prime mole percent of structure (II) is from 99.5 to 50, and when R_1 is group (v), there are at least three units having structure (I) and at least 40 units having structure (II).

2. A laminate according to claim 1 wherein the polysiloxane is present in an amount effective to decrease the zero peel value (as determined by any of the tests herein described) of the laminate by at least 25 percent from the zero peel value of a control laminate from which the polysiloxane is absent.

3. A laminate according to claim 1 or 2 wherein the polysiloxane is present in an amount effective to produce in the tests as hereinbefore described a zero peel value of less than 600 grams on a stainless steel test surface and less than 500 grams on acrylic and SBR test surfaces.

4. A laminate according to claim 1, 2 or 3 wherein the amount of polysiloxane is at least 0.002 grams per square meter on a dry weight basis.

5. A laminate according to claim 4 wherein the amount of polysiloxane is in the range from 0.002 to 1.0 gram per square meter on a dry weight basis.

6. A laminate according to any preceding

claim wherein R_1 is phenyl, and R_2, R_3 and R_4 are methyl.

7. A laminate according to claim 6 wherein the prime mole percent of structure (I) is from 0.5 to 30 and the prime mole percent of structure (II) is from 99.5 to 70.

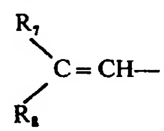
8. A laminate according to claim 7 wherein the prime mole percent of structue (I) is about 4.5 and the prime mole percent of structure (II) is about 95.5.

9. A laminate according to claim 6, 7 or 8 wherein the polysiloxane possesses a number average molecular weight of from 25,000 to 250,000.

10. A laminate according to any one of claims 1 to 5 wherein R_1 is phenyl, R_2 is phenyl, and R_3 and R_4 are methyl.

11. A laminate according to any one of claims 1 to 5 wherein R_1 is methyl, the prime mole percents of structures (I) and (II) are equal, and the polysiloxane possesses a viscosity in the range from 60×10^3 to 20×10^6 cps.

12. A laminate according to any one of claims 1 to 5 wherein R_1 is



and R_7 and R_8 are H, the prime mole percent of structure (I) is from 40.0 to 60.0 and the prime mole percent of structure (II) is from 60.0 to 40.0, and the polysiloxane possesses a number average molecular weight in the range from 5×10^5 to 1×10^6.

13. A laminate according to any one of claims 1 to 5 wherein R_1 is polyoxalkylene and R_2, R_3 and R_4 are methyl and the viscosity of the polysiloxane is about 2250 cps.

14. A laminate according to any one preceding claim wherein the amount of the pressure sensitive adhesive is in the range from 0.5 to about 8.0 mg/cm^2.

15. A laminate according to any preceding claim wherein the pressure sensitive adhesive is a water-based acrylic-vinylacetate copolymeric or water-based polybutylacrylate adhesive; or an organic solvent-based acrylic-vinyl acetate copolymeric adhesive.

16. A laminate according to any one preceding claim wherein the facing layer is of knitted, woven or nonwoven textile fabric, metal foil, wood veneer paper, a continuous film of polymeric plastics material, or a film of such a plastics polymer having a metallic coating thereon.

17. A laminate according to any one preceding claim wherein the facing layer is composed of a decorative layer and a transparent protective layer.

18. A laminate according to any preceding claim wherein the discontinuous polysiloxane layer is an interlayer between the layer of adhesive and the release surface of a releasable backing layer.

19. A laminate according to claim 18 in the form of tile appliques, decorative wall covering, floor covering, labels, decals, tapes, or shelf edging.

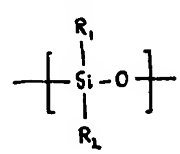
20. A laminate according to any one of claims 1 to 17 in roll form, the other surface of the facing layer being a release surface and the discontinuous polysiloxane layer being an interlayer between the layer of adhesive and the release surface.

21. A laminate according to any one of claims 18, 19 or 20 wherein the release surface has been treated with a release material.

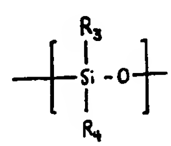
22. A laminate according to claim 21 wherein the release material is a silicone coating.

23. A stack of a plurality of sheets, each sheet being a laminate according to any one of claims 1 to 17, the other surface of each facing layer being a release surface, and the sheets being stacked such that the discontinuous polysiloxane layer of one sheet is an interlayer between the adhesive layer of the one sheet and the release surface of the next adjacent sheet.

24. A method for making a laminate wherein a release surface on a first sheet is coated with a discontinuous uniformly distributed, layer of a polysiloxane and then with a pressure sensitive adhesive to form a first laminate, the first laminate is subjected to conditions suitable to dry or cure the pressure sensitive adhesive, and the pressure sensitive adhesive side of the thus treated first laminate is married to one surface of a facing layer, said polysiloxane consisting of monomeric units having structures (I) and (II)

(I) 

and.

(II) 

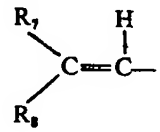
wherein

R_1 is:

(i) phenyl;

(ii) methyl;

(iii) tolyl;

(iv) 

wherein R_7 and R_8 are the same or different and are hydrogen, methyl, or ethyl; or

(v) polyoxalkylene having the structural formula

$$-R_5(OC_2H_4)_n(OC_3H_6)_mOR_6$$

wherein R_5 is an alkylene group having at least two carbon atoms, R_6 is a monovalent hydrocarbon group having from 1 to 10 carbon atoms, n and m are integers the sum of which is such that the oxyalkylene block

$$R_6O(C_3H_6O)_m(C_2H_4O)n$$

has a molecular weight of at least 1500 and from 15 to 60 weight percent of the oxyalkylene units are oxyethylene units, and wherein the oxyalkylene block constitutes from 85 to 30 weight percent of the polysiloxane polymer;

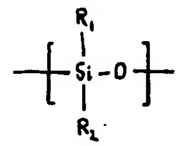
R_2 is methyl, ethyl, or phenyl; and

R_3 and R_4 are the same or different and are methyl or ethyl;

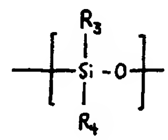
with the proviso that when R_1 is group (i), (ii), (iii) or (iv), the prime mole percent of structure (I) is from 0.5 to 50 and the prime mole percent of structure (II) is from 99.5 to 50, and when R_1 is group (v), there are at least three units having structure (I) and at least 40 units having structure (II).

25. A method according to claim 24, wherein the other surface of the facing layer possesses release properties and wherein, subsequent to the marrying step, the first sheet is peeled from said thus treated first laminate to form a second laminate composed of the facing layer, the pressure sensitive adhesive layer and the polysiloxane layer, and wherein the second laminate is rolled upon itself such that the polysiloxane layer is next to the other surface of the facing layer.

26. A method for making a laminate wherein a facing layer is coated with a layer of a pressure sensitive adhesive to form a first laminate, the first laminate is subjected to conditions suitable to cure or dry the pressure sensitive adhesive, the pressure sensitive adhesive side of the thus treated first laminate is coated with a discontinuous, uniformly distributed, layer of a polysiloxane and then married to a release surface, said polysiloxane consisting of monomeric units having structure (I) and (II)

(I) 

and

(II) 

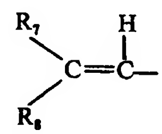
wherein

R_1 is:

(i) phenyl;

(ii) methyl

(iii) tolyl;

(iv) 

wherein R_7 and R_8 are the same or different and are hydrogen, methyl, or ethyl; or

(v) polyoxalkylene having the structural formula

$$-R_5(OC_2H_4)_n(OC_3H_6)_mOR_6$$

wherein R_5 is an alkylene group having at least two carbon atoms, R_6 is a monovalent hydrocarbon group having from 1 to 10 carbon atoms, n and m are integers the sum of which is such that the oxyalkylene block

$$R_6O(C_3H_6O)_m(C_2H_4O)n$$

has a molecular weight of at least 1500 and from 15 to 60 weight percent of the oxyalkylene units are oxyethylene units, and wherein the oxyalkylene block constitutes from 85 to 30 weight percent of the polysiloxane polymer;

R_2 is methyl, ethyl, or phenyl; and

R_3 and R_4 are the same or different and are methyl or ethyl;

with the proviso that when R_1 is group (i), (ii), (iii) or (iv), the prime mole percent of structure (I) is from 0.5 to 50 and the prime mole percent of structure (II) is from 99.5 to 50, and when R_1 is group (v), there are at least three units having structure (I) and at least 40 units having structure (II).

27. A method according to claim 26 wherein the other surface of the facing layer is the release surface and the marrying step is carried out by rolling said thus

treated first laminate upon itself such that the polysiloxane layer is next to the other surface of the facing layer.

28. A method according to claim 26 wherein the outer surface of the facing layer is the release surface and wherein the marrying step is carried out by cutting said thus treated laminate into separate, essentially equally-sized pieces and stacking one piece upon another such that the polysiloxane layer of one piece is next to the other surface of the facing layer of the next piece in the stack.

29. A method according to any one of claims 24 to 28 wherein the polysiloxane is coated in an amount effective to decrease the zero peel value (as determined by any of the tests herein described) of the laminate by at least 25 percent from the zero peel value of a control laminate from which the polysiloxane is absent.

30. A method according to any one of claims 24 to 29 wherein the polysiloxane is applied in an amount effective to produce in the tests as hereinbefore described a zero peel value of less than 600 grams on a stainless steel test surface and less than 500 grams on acrylic and SBR test surfaces.

31. A method according to any one of claims 24 to 30 wherein the amount of polysiloxane coated is in the range from 0.002 to 1.0 gram per square meter on a dry weight basis.

32. A method according to any one of claims 24 to 31 wherein the facing layer is of knitted, woven or non woven textile fabric, metal foil, wood veneer, paper a continuous film of polymeric plastics material, or a film of such a plastics polymer having a metallic coating thereon.

33. A method according to any one of claims 24 to 32, wherein the facing layer is itself composed of a bottom decorative layer and a top, transparent protective layer.

34. A method according to any one of claims 24 to 33, wherein a solution of the polysiloxane is applied to the release surface and thereafter the solvent is removed from the applied polysiloxane.

35. A method according to claim 34, wherein the concentration of the polysiloxane in the solution is from 0.125 to 15 weight based on the weight of the solution.

36. A method according to any one of claims 24 to 33, wherein the polysiloxane is applied in the form of an aqueous emulsion.

37. A method according to any one of claims 24 to 36 wherein R_1 is phenyl, and R_2, R_3, and R_4 are methyl.

38. A method according to claim 37 wherein the prime mole percent of structure (I) is from 0.5 to 30 and the prime mole percent of structure (II) is from 99.5 to 70.

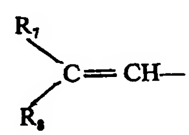
39. A method according to claim 38 wherein the prime mole percent of structure (I) is about 4.5 and the prime mole percent of structure (II) is about 95.5.

40. A method according to claim 37, 38 or 39, wherein the molecular weight of the polysiloxane is from about 25,000 to about 250,000.

41. A method according to any one of claims 24 to 36 wherein R_1 is phenyl, R_2 is phenyl, and R_3 and R_4 are methyl.

42. A method according to any one of claims 24 to 36 wherein R_1 is methyl, the prime mole percents of structure (I) and (II) are equal and the viscosity of the polysiloxane is in the range from 60×10^3 to 20×10^6 cps.

43. A method according to any one of claims 24 to 36 wherein R_1 is



and R_7 and R_8 are H, the prime mole percent of structure (I) is from 40.0 to 60.0 and the prime mole percent of structure (II) is from 60.0 to 40.0, and the polysiloxane possesses a molecular weight from 5×10^5 to 1×10^6.

44. A pressure sensitive adhesive coated laminate substantially as described with reference to the accompanying drawings or to any of the Examples herein.

45. A method of making a pressure sensitive adhesive coated laminate substantially as described with reference to the accompanying drawings or to any of the Examples herein.

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FIG.1

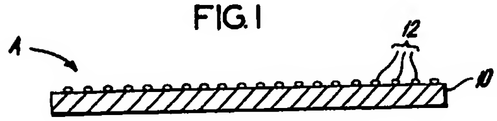


FIG.2

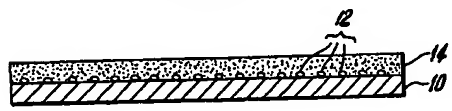


FIG.3

facing layer (protective)

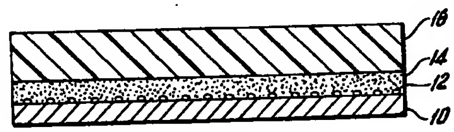


FIG.4

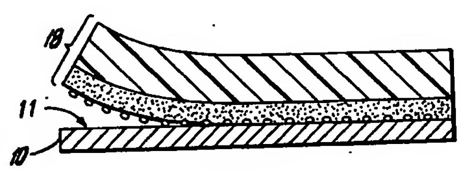


FIG.5

1541311 COMPLETE SPECIFICATION

11 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 2

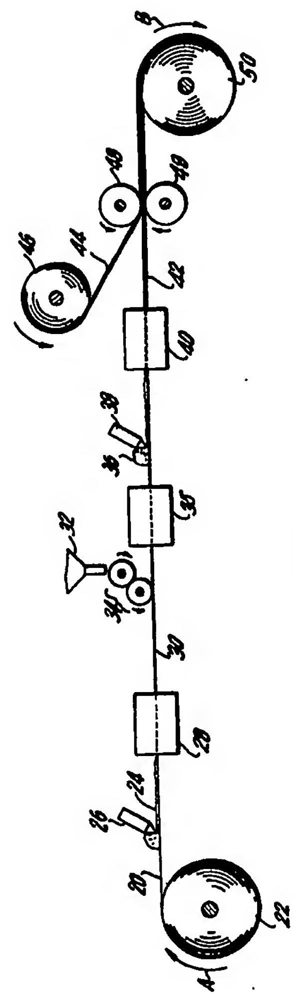


FIG.6

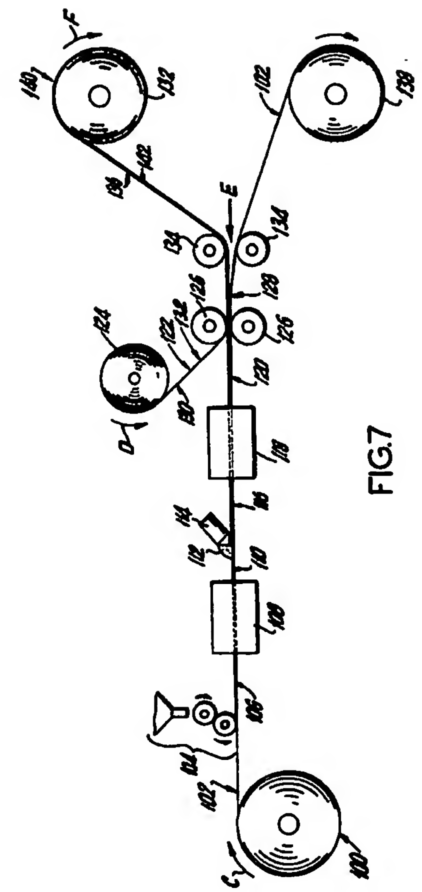


FIG.7

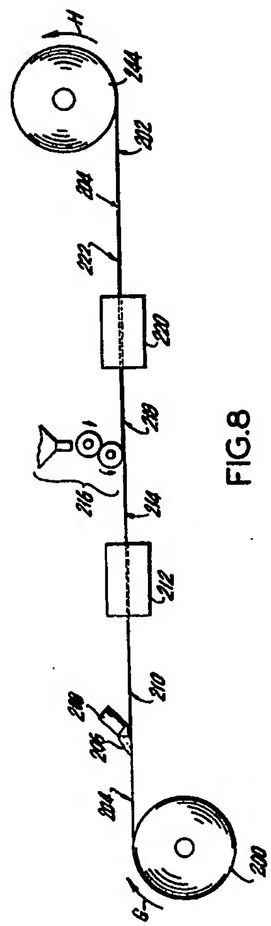


FIG.8

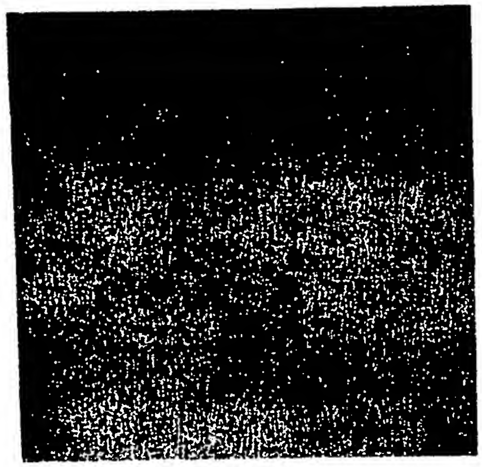


FIG. 9

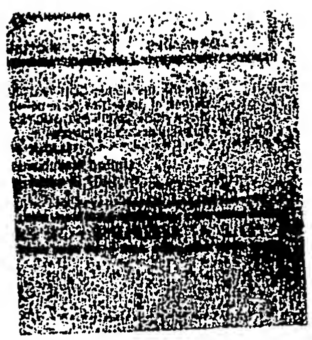


FIG. 10

FIG.11

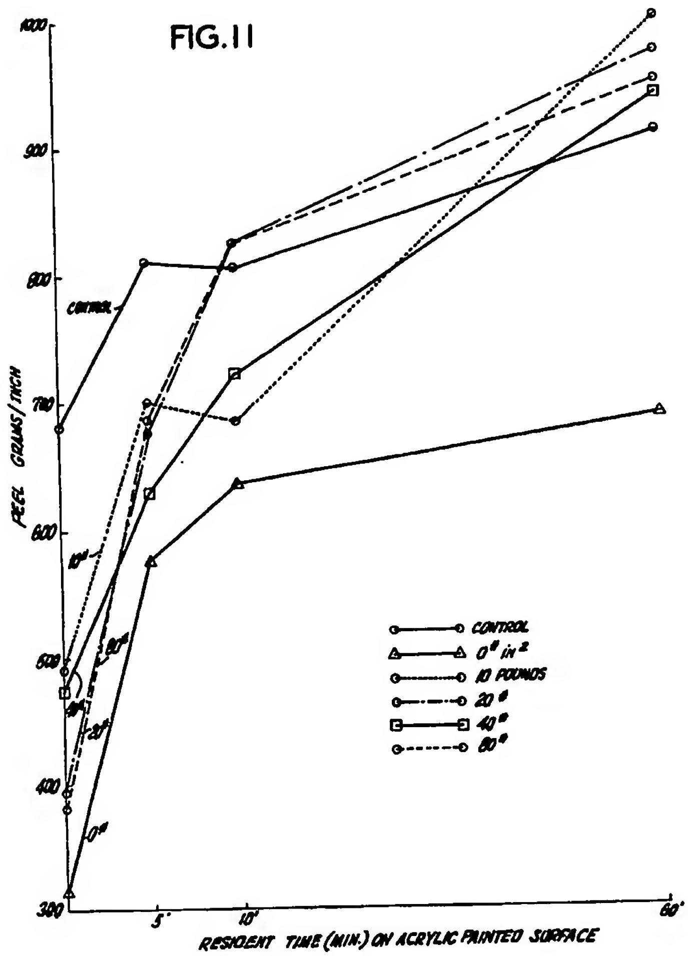
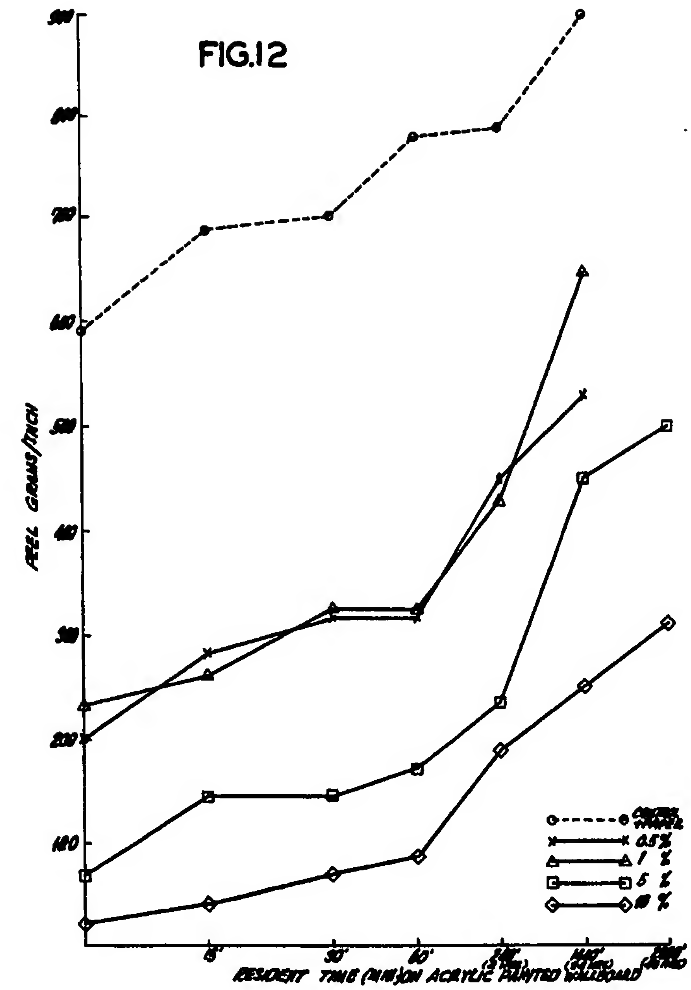

1000
900
800
700
600
500
400
300
PEEL GRAMS/INCH
CONTROL
10#
20#
40#
80#
0#
5'
10'
60'
RESIDENT TIME (MIN.) ON ACRYLIC PAINTED SURFACE
CONTROL
0# IN²
10 POUNDS
20#
40#
80#

FIG.12


PEEL GRAMS/INCH
200
300
400
500
600
700
800
900
15'
30'
60'
RESIDENT TIME (MIN) ON ACRYLIC PAINTED WALLBOARD
0.5%
1 %
5 %

1541311 COMPLETE SPECIFICATION

11 SHEETS This drawing is a reproduction of the Original on a reduced scale

Sheet 8

FIG.13

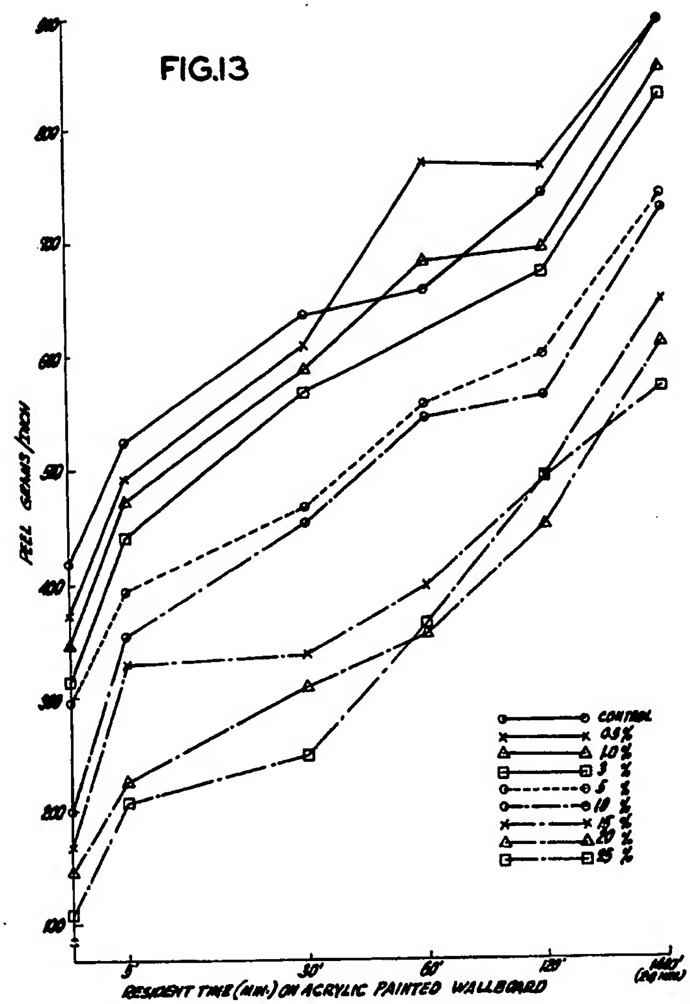


FIG.14

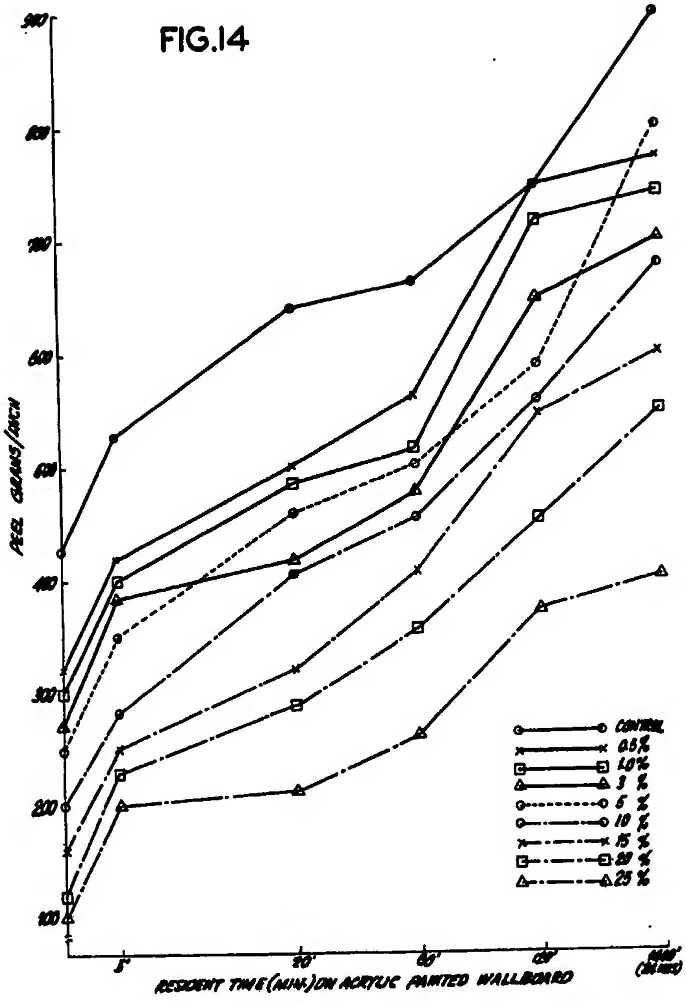
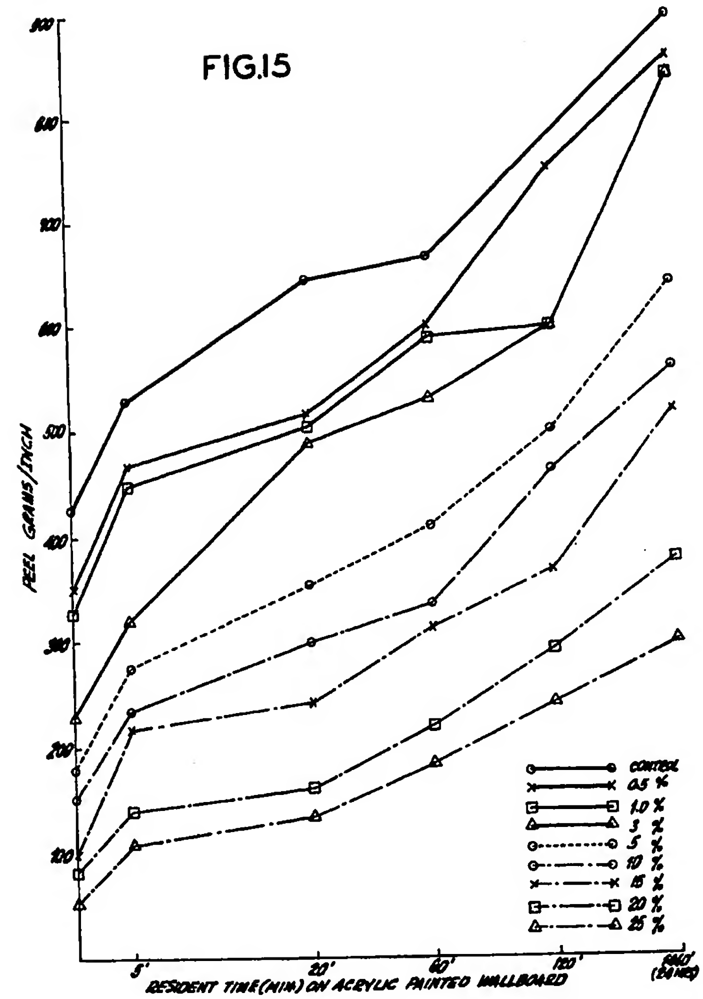

PEEL GRAMS/INCH
900
800
700
600
500
400
300
200
100
RESIDENT TIME (MIN.) ON ACRYLIC PAINTED WALLBOARD
5'
30'
60'
120'
CONTROL
0.5%
1.0%
3 %
5 %
10 %
15 %
20 %
25 %

FIG.15


PEEL GRAMS/INCH
500
400
300
200
100
CONTROL
0.5 %
1.0 %
3 %
5 %
10 %
15 %
20 %
25 %
5'
20'
60'
120'
RESIDENT TIME (MIN) ON ACRYLIC PAINTED WALLBOARD

1541311 COMPLETE SPECIFICATION

11 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 11

FIG.16